



Ta–O–C chemical bond enhancing charge separation between Ta⁴⁺ doped Ta₂O₅ quantum dots and cotton-like g-C₃N₄



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ABSTRACT

We successfully synthesized a novel Ta⁴⁺ self-doped Ta₂O₅ quantum dots and the self-doped Ta₂O₅ quantum dots modified cotton-like g-C₃N₄ nanosheet (TCN) by vapor hydrolysis reaction and calcining treatment. The as-prepared Ta₂O₅ showed excellent visible light response from 400 to 800 nm, mainly because the formation of Ta⁴⁺ species, which was confirmed by EPR and XPS technology. The estimated bandgap of the self-doped Ta₂O₅ was ~2.78 eV, which was much lower than that of the commercial Ta₂O₅ (~4.0 eV), and the visible light photocatalytic activity of the self-doped Ta₂O₅ for hydrogen production was about 7.98 μmol g⁻¹ h⁻¹. The photocatalytic activity of TCN photocatalyst for hydrogen production and RhB degradation was highly enhanced under visible light irradiation compared with those of g-C₃N₄ and the self-doped Ta₂O₅, indicating the higher charge separation efficiency, which was further confirmed by the photocurrent transient response, electrochemical impedance spectra and PL emission spectra. And the hydrogen evolution rate and the degradation rate constant for RhB degradation of TCN photocatalyst could reach 624.99 μmol g⁻¹ h⁻¹ and 0.1512 min⁻¹, which were about 3.7 and 11.9 times higher than those of pure g-C₃N₄, and 78.29 and 283.78 times higher than those of the self-doped Ta₂O₅, much higher than those of the simple physical mixture. The active species trapping experiment of TCN photocatalyst showed that RhB degradation was mainly attributed to the direct hole oxidation. Besides, the XPS results further confirmed that Ta–O–C chemical bond was formed between the as-prepared Ta₂O₅ and cotton-like g-C₃N₄. It was the strong synergistic interactions of Ta–O–C chemical bond and Ta⁴⁺ defect energy level that highly enhanced the photocatalytic activities of TCN catalyst for the hydrogen production and RhB degradation.

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1. Introduction

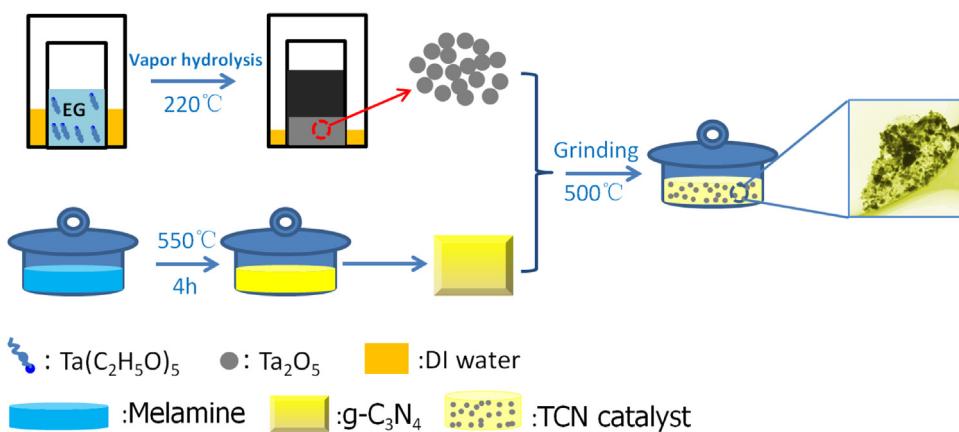
Recently, more attentions have been attracted on the charge separation of the semiconductor photocatalyst for solar energy conversion and pollutant degradation since Fujishima and Honda first discovered that water could be decomposed into hydrogen and oxygen in 1972 [1]. And it is indeed a profitable and promising attempt to relieve the energy crisis and environmental pollution using photocatalysis technology [2–4]. In general, semiconductor is expected to highly accelerate the rate of photocatalytic reaction for solar energy conversion and pollutant degradation [5,6]. However, unlike the nature enzyme catalysts, artificial photocatalysts always suffer from some disadvantages, such as the low charge separa-

tion efficiency, inefficient photocatalytic activity, limited spectral response range and poor photocatalysis stability [7,8]. And therefore, it is urgent for researchers to put insights into the studies of photocatalytic mechanisms by the theoretical calculation and exploit new types of photocatalysts to enhance the charge separation efficiency and extend the spectral response range [9,10]. Until now, fabricating heterojunction photocatalyst is still an effective strategy, which benefits the wide bandgap semiconductors with intriguing visible light response.

Tantalic oxide (Ta₂O₅), a typical wide bandgap semiconductor, is a potential and promising photocatalyst in photocatalytic water splitting and pollutant removal. The valence band and conduction band of Ta₂O₅ were reported to be about -0.17 and +3.83 eV [11], respectively. Thus, it is of great difficulty for wide bandgap Ta₂O₅ to have visible light photocatalytic activity because of its wide bandgap (~4.0 eV) [12]. Consequently, it is a highly desirable attempt to explore novel Ta₂O₅ catalysts with visible light response.

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Scheme 1. Schematic illustration of the formation of the self-doped Ta_2O_5 quantum dots and TCN catalysts.

Besides, some researches performed by Xu et al. [13] and Wang et al. [14] showed that fabricating novel heterojunction photocatalyst could contribute to enhance the charge separation and extend the spectral response range. And the novel self-doped Ta_2O_5 might also have efficient charge separation efficiency and wide spectral response range.

Graphite carbon nitride ($\text{g-C}_3\text{N}_4$), a novel type of metal-free visible-light semiconductor catalyst, could be obtained from different precursors, including melamine, urea, thiourea, etc [15–17]. Until now, $\text{g-C}_3\text{N}_4$ has been applied for CO_2 reduction [18], pollutant removal [19], and hydrogen production from water decomposition [20], mainly because of its suitable electronic structure [21,22]. However, the photocatalytic activities of $\text{g-C}_3\text{N}_4$ prepared by the traditional methods are not very high because of its lower specific surface area and more defects [23,24]. Some researches on modifying $\text{g-C}_3\text{N}_4$ have been performed to enhance the photocatalytic activities, such as $\text{Bi}/\text{g-C}_3\text{N}_4$ [25], $\text{Au}/\text{Pt}/\text{g-C}_3\text{N}_4$ [26], $\text{CeO}_2/\text{g-C}_3\text{N}_4$ [27], $\text{AgX}/\text{g-C}_3\text{N}_4$ [28], etc. The photocatalytic activities of these $\text{g-C}_3\text{N}_4$ -based composites were highly enhanced to compare with those of pristine $\text{g-C}_3\text{N}_4$. The valence band and conduction band of $\text{g-C}_3\text{N}_4$ are about -0.90 and $+1.80$ eV [15,23]. And thus, it is likely to form new heterostructure between cotton-like $\text{g-C}_3\text{N}_4$ and the self-doped Ta_2O_5 to promote the charge separation because of the well matched band structures [27].

In this work, we successfully prepared a novel Ta^{4+} self-doped Ta_2O_5 quantum dots and TCN catalysts by vapor hydrolysis reaction and calcining treatment for the first time. The photocatalytic activities for hydrogen production and RhB photodegradation of TCN catalyst were highly enhanced mainly because of the formation of $\text{Ta}-\text{O}-\text{C}$ chemical bond, which highly enhanced the charge separation between the self-doped Ta_2O_5 and cotton-like $\text{g-C}_3\text{N}_4$. The possible direct Z-scheme mechanisms of TCN catalyst for hydrogen production and RhB degradation were also investigated in detail.

2. Experimental

2.1. Sample preparation

All the chemicals were commercially available and directly used without any treatment. The self-doped Ta_2O_5 quantum dots were prepared by vapor hydrolysis reaction in this experiment. In a typical procedure, 8 mL distilled water was added into a Teflon line, and 0.50 g $\text{Ta}(\text{C}_2\text{H}_5\text{O})_5$ was dissolved in 6 mL ethylene glycol in an inner container and transferred into the Teflon line. Then the autoclave was sealed and heated at 220 °C for 20 h. The product was separated from some impurity and ethylene glycol by centrifugation, washed

with ethanol and distilled water several times, and then dried at ~ 60 °C for 48 h.

The $\text{g-C}_3\text{N}_4$ was fabricated by calcining treatment according to the literature with slight modifications [15]. Typically, melamine was put into a covered ceramic crucible and heated to 550 °C at a rate of 0.5 °C/min in a muffle furnace for 4 h, naturally cooled, and then the $\text{g-C}_3\text{N}_4$ was obtained.

TCN catalysts were successfully prepared by a facile calcining method. At first, the as-prepared $\text{g-C}_3\text{N}_4$ with different amount of the self-doped Ta_2O_5 quantum dots were mixed and grinded, then the mixtures were transferred into a ceramic crucible with a cover and heated at 500 °C at a heating rate of 2 °C/min for 3 h, naturally cooled, then TCN catalyst was obtained. The samples with the different mass ratio ($\text{g-C}_3\text{N}_4/\text{Ta}_2\text{O}_5$) of 1:1, 4:1, 6:1 and 8:1 were denoted as TCN-1, TCN-4, TCN-6, and TCN-8, respectively. For comparison, the mixed sample with mass ratio ($\text{g-C}_3\text{N}_4/\text{Ta}_2\text{O}_5$) of 6:1 without calcining treatment was denoted as TCN-mix. And Scheme 1 showed the formation procedure of self-doped Ta_2O_5 quantum dots and TCN catalyst.

2.2. Characterization

The morphologies of $\text{g-C}_3\text{N}_4$ and TCN-6 photocatalyst were investigated by cold field emission Scanning electron microscope (SEM) (Hitachi, SU8010) and Transmission electron microscope (TEM) (Tecnai, G2F30) and HRTEM at 300 kV. The crystal structure was investigated by X-ray diffraction (XRD) (PANalytical, X'Pert PRO) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). The chemical structure and the element chemical states of the as-prepared Ta_2O_5 and TCN catalyst were studied on a Fourier-transform infrared spectroscopy (FT-IR) (Thermo Nicolet Corporation, Avatar 360) and X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, ESCALAB 250Xi). The UV-vis absorption spectra of commercial Ta_2O_5 , the self-doped Ta_2O_5 , $\text{g-C}_3\text{N}_4$ and TCN catalysts were determined by double-beam ultraviolet-visible spectrophotometer (Beijing's general instrument co., LTD, TU-1900) with BaSO_4 as reference standard. Photoluminescence emission spectra (PL) was carried out on a FluoroMax-4 photoluminescence instrument (HORIBA Jobin Yvon) with $\text{g-C}_3\text{N}_4$, and the self-doped Ta_2O_5 quantum dots and TCN catalysts were dissolved in ethyl alcohol and treated by ultrasound for 30 min. The uncoupled electron properties of commercial Ta_2O_5 , $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 and TCN catalysts were investigated on an Electron paramagnetic resonance spectrometer (EPR) (at 90 K (Bruker Corporation, A300-10/12)).

2.3. Photocatalytic hydrogen production

Photocatalytic hydrogen production tests were conducted under 300 W Xe lamp using a 420 nm cut-off filter. The reaction was conducted in a sealed gas circulation and evacuation system (LabSolar-III AG, Beijing PerfectLight Co., Ltd., China). The reactor was placed under the Xe lamp for photocatalytic experiment. In a typical procedure, 0.05 g TCN catalyst with 3 wt.% Pt co-catalyst was added into a mixture of 10 mL triethanolamine (TEOA) and 90 mL distilled water. After sealing the reactor and the pressure achieving a balance, the reactor was then irradiated for 60 min to photodeposit $\text{H}_2\text{PtCl}_6\cdot(\text{H}_2\text{O})_6$ onto TCN catalyst by a 300 W Xe lamp (PLS SXE300C, Beijing PerfectLight Co., Ltd., China). Then pumping the H_2 produced in the photodeposition process and the pressure achieving a balance again, the reactor was irradiated by 300 W Xe lamp (MicroSolar300) using a 420 nm cut-off filter for 120 min. The amount of hydrogen production was measured by gas chromatograph (Techcomp, 7890 II) with a TCD detector (molecular sieve 5 Å column) and Ar as carrier gas. The hydrogen production activity of the self-doped Ta_2O_5 was measured under 300 W Xe lamp using a 400 nm cut-off filter with 3 wt.% Pt co-catalyst.

2.4. Photodegradation experiment

The photocatalytic activities of TCN catalysts for RhB degradation were evaluated under visible light irradiation using a 300 W Xe lamp (MicroSolar 300, Beijing PerfectLight Co., Ltd., China) with a 420 nm cut-off filter. In a typical procedure, 0.10 g TCN catalyst was mixed with RhB solution (10 mg/L) and stirred for 30 min in the dark to achieve an adsorption–desorption equilibrium. Then the reaction system was irradiated using a 300 W Xe lamp (MicroSolar300) with a 420 nm cut-off filter and the reaction solution was collected every 10 min for analyzing by UV–vis spectrophotometer (Shanghai Spectrum Instruments Co., Ltd, 722E). The recyclable photocatalytic activity test was also carried out, and the photocatalyst was collected by centrifuging after each run, and used for next run. Besides, the trapping experiments of TCN-6 catalyst with addition of 0.1 g ammonium oxalate or 2 mL isopropanol for RhB degradation were also carried out to investigate the main active species under visible light irradiation ($\lambda > 420$ nm).

2.5. Photoelectrochemical tests

The photocurrent transient response and electrochemical impedance spectra of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 and TCN-6 catalysts were determined on a CHI660D electrochemical working station (shanghai, Chen hua) with a three-compartment cell. A 300 W Xe lamp (PLS SXE300C) with a 420 nm cutoff filter was employed as the visible light resource. The electrodes of the catalysts, Ag/AgCl electrode and Pt wire electrode were as the working electrode, counter electrode and reference electrode, respectively, and 0.1 M Na_2SO_4 solution was served as electrolyte. The electrode was prepared by an electrophoretic deposition method with slight modifications [29]. 25 mg catalyst was dispersed in 50 mL isopropyl alcohol with a small amount of $\text{Mg}(\text{NO}_3)_2$ (0.0074 g) and treated with ultrasound for 30 min. The ITO glass was used as working electrode with a Pt sheet as counter electrode. The electrophoretic deposition was carried out for 3 min with a 50 V direct-current voltage, and then the prepared electrode was naturally dried at room temperature for use.

3. Result and discussion

The morphologies and nanostructure of pure $\text{g-C}_3\text{N}_4$ and TCN-6 catalyst were investigated via SEM, TEM and HRTEM. As depicted in Fig. 1(a), pure $\text{g-C}_3\text{N}_4$ was a typical block-shaped morphology

with layered structures. The size of $\text{g-C}_3\text{N}_4$ grain was approximately 2–3 μm . Fig. 1(b) also clearly revealed the surface morphology of $\text{g-C}_3\text{N}_4$. The insert in Fig. 1(b) confirmed the formation of $\text{g-C}_3\text{N}_4$. Fig. 1(c) showed the microscopic morphology of TCN-6 catalyst with a relatively homogeneous distribution of Ta_2O_5 nanoparticle incorporated in the cotton-like $\text{g-C}_3\text{N}_4$, appearing as the soft cotton-like $\text{g-C}_3\text{N}_4$ modified by the self-doped Ta_2O_5 . The laminar cotton-like $\text{g-C}_3\text{N}_4$ contributed to the increase of the specific surface area [30]. As depicted in Fig. 1(d), the HRTEM image of the TCN-6 catalyst showed an interplanar spacing of 0.386 nm with the particle size of the self-doped Ta_2O_5 less than 10 nm, which was ascribed to the (001) crystal interplanar of Ta_2O_5 and further confirmed the formation of the self-doped Ta_2O_5 quantum dots. Besides, the high magnification TEM images of TCN-6 catalyst in Fig. S1 (b) also confirmed the existence of Ta_2O_5 quantum dots in the TCN catalyst. The inset of electron diffraction of Fig. 1(d) clearly revealed the poor crystallization of TCN-6 catalyst. Fig. 1(e, f) showed the high-angle annular dark field and the scanning transmission electron (HAADF-STEM) image and the corresponding elemental mapping of TCN-6 catalyst. Fig. 1(e) further revealed the cotton-like morphology of TCN catalyst, which was consistent with the SEM image of TCN-6 catalyst in Fig. S1 (a). Fig. 1(f) clearly revealed that TCN-6 catalyst was composed of carbon, nitrogen, oxygen and tantalum elements, which were uniformly distributed over the entire TCN-6 catalyst, indicating the relatively homogeneous distribution of the self-doped Ta_2O_5 over the cotton-like $\text{g-C}_3\text{N}_4$.

Fig. 2 showed the XRD patterns of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 , TCN-1, TCN-4, TCN-6 and TCN-8 catalysts. The XRD pattern of $\text{g-C}_3\text{N}_4$ showed two distinct diffraction peaks at around 13.0° and 27.4°, which were indexed for the (100) and (002) planes of $\text{g-C}_3\text{N}_4$ [23,31], corresponding to the in-plane structural packing motif of tris-triazine units and inter-planar stacking peak of aromatic system [32]. The XRD pattern of the self-doped Ta_2O_5 showed one distinct and broad diffraction peaks at around 22.9°, corresponding to the (001) plane of Ta_2O_5 (JCPDS No.25-0922), which was in good agreement with HRTEM results and further confirmed the formation of Ta_2O_5 . The other diffraction peaks were slightly weaker for Ta_2O_5 because of its relatively poor crystallinity under the low reaction temperature, but the characteristic diffraction peaks of Ta_2O_5 existed, and well agreed with the standard card of JCPDS No.25-0922. The average crystallite size of the self-doped Ta_2O_5 was 8.92 nm according to Debye–scherer's equation, further confirming the formation of the self-doped Ta_2O_5 quantum dots, which was also consistent with the HRTEM results. The diffraction peaks of $\text{g-C}_3\text{N}_4$ and Ta_2O_5 were also observed in TCN-1, TCN-4, TCN-6 and TCN-8 catalysts. The relative diffraction intensity of (100) and (002) planes of $\text{g-C}_3\text{N}_4$ became stronger with the mass ratio increase of $\text{g-C}_3\text{N}_4$, while the relative diffraction peak intensity of (001) plane of Ta_2O_5 increased with the decreasing of the mass ratio of $\text{g-C}_3\text{N}_4$ regularly. The regular changes of the diffraction intensity had been reported for $\text{BiVO}_4/\text{g-C}_3\text{N}_4$ [33] and $\text{CeO}_2/\text{g-C}_3\text{N}_4$ [27]. And we might conclude the coupling of (100) and (002) planes of $\text{g-C}_3\text{N}_4$ and (001) planes of the self-doped Ta_2O_5 established a closely interface [27,34], which was also consistent with the HRTEM analyses. And thus, the above analyses further confirmed the formation of TCN catalyst.

Fig. 3 showed the FT-IR spectra of the self-doped Ta_2O_5 , $\text{g-C}_3\text{N}_4$, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts. The absorption peak of the self-doped Ta_2O_5 at 3460 cm^{-1} could be attributed to the –OH of carbon materials or the absorbed water molecules [35,36]. The broad absorption peak of $\text{g-C}_3\text{N}_4$ at 3150 cm^{-1} was ascribed to the stretching vibration of N–H and O–H derived from melamine polymerization and absorbed water molecule, respectively [36,37]. The absorption peaks at 2931 and 2877 cm^{-1} was assigned to the skeletal vibration of sp^2 and sp^3 C–H [38,39]. The

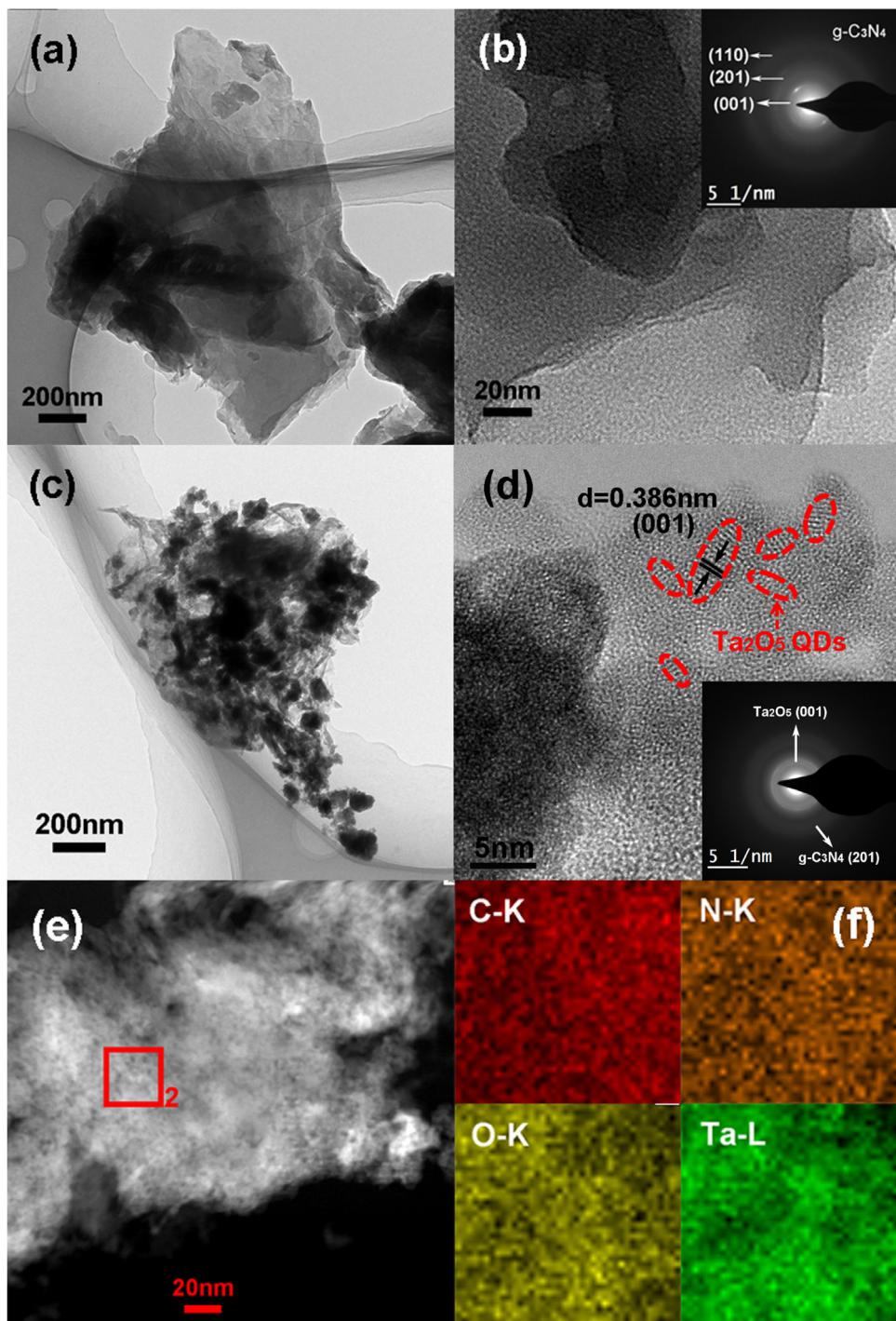


Fig. 1. Typical TEM, HRTEM images of $\text{g-C}_3\text{N}_4$ (a, b) and TCN (c, d) catalysts; HAADF-STEM image (e) and the corresponding EDS mapping (f) of TCN catalyst.

peak located at 1593 cm^{-1} was attributed to the hydrogen-bonded carbonyl stretching, indicating the formation of carbon-related compounds in the vapor hydrolysis reaction. The absorption peaks at $850\text{--}1800\text{ cm}^{-1}$ was attributed to the typical stretching vibration of CN heterocycles [27]. The peak at 808 cm^{-1} was attributed to the breathing mode of triazine units [31], which further confirmed the formation of $\text{g-C}_3\text{N}_4$. The broad absorption peak at 645 cm^{-1} was attributed to the combination of Ta—O and Ta—O-Ta bonds vibrations [35,40,41]. For TCN catalyst, the broad absorption band at 645 cm^{-1} of Ta—O-Ta and Ta—O confirmed the existence of Ta_2O_5 in the as-prepared TCN catalysts [35,40–42]. And the broad absorption

band for TCN-1, TCN-4, TCN-6 and TCN-8 catalysts at 645 cm^{-1} had a slight red shift with the mass ratio increasing of the self-doped Ta_2O_5 [33,37]. It was obviously that the absorption peak intensity of triazine units at 808 cm^{-1} of TCN-1, TCN-4, TCN-6 and TCN-8 catalysts increased regularly with the mass ratio increase of $\text{g-C}_3\text{N}_4$. And thus, it could be concluded that TCN catalyst was successfully fabricated using $\text{Ta}(\text{C}_2\text{H}_5\text{O})_5$ and melamine as the precursors.

Fig. 4 showed the high-resolution XPS spectra of C1s, N1s, O1s and Ta 4f to further investigate the elemental chemical states and composition of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 and TCN catalyst. As shown in Fig. 4(a), the C1s peak for Ta_2O_5 at 284.7 eV was ascribed

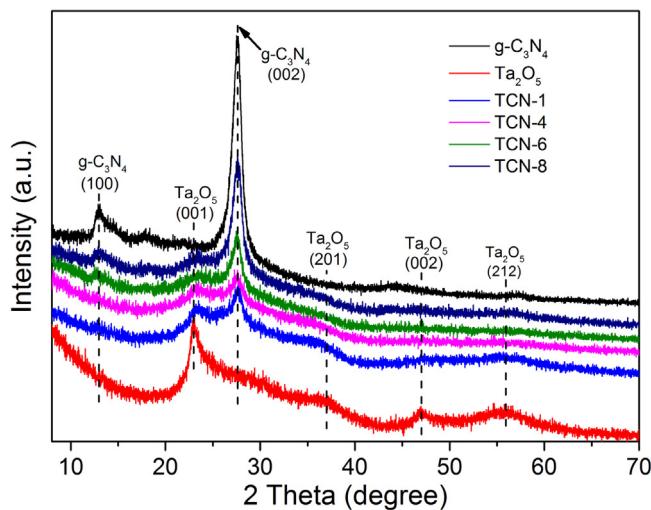


Fig. 2. XRD patterns of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 , and TCN catalysts.

to adventitious carbon [43], and the peak at 286.0 eV was attributed to the carbon-compounds, seeming like carbon in the graphite intercalation compounds produced from ethylene glycol [35,44], which might be in favour of visible light absorption for the self-doped Ta_2O_5 , and the similar phenomenon was reported in carbon modified NaTaO_3 mesocrystal [35]. The C1s peaks at 284.9 eV for pure $\text{g-C}_3\text{N}_4$ and TCN-6 catalysts were ascribed to surface adventitious carbon, and the peaks at 288.6 and 288.4 eV for pure $\text{g-C}_3\text{N}_4$ and TCN-6 were ascribed to the sp^2C bonded in $\text{N}-\text{C}=\text{N}$ of $\text{g-C}_3\text{N}_4$ [45]. In Fig. 4(b), the N1s peaks for $\text{g-C}_3\text{N}_4$ at 398.9, 399.9 and 401.5 eV could be assigned to the pyridinic-like nitrogen ($\text{N}-\text{sp}^2\text{C}$), graphitic nitrogen ($\text{N}-(\text{C})_3$) and amino groups ($\text{C}-\text{N}-\text{H}$), respectively [27,37]. The N1s of TCN-6 catalyst displayed slightly lower binding energies (398.8, 399.8 and 401.3 eV) compared with those of $\text{g-C}_3\text{N}_4$ because of the strong interaction between Ta_2O_5 and $\text{g-C}_3\text{N}_4$ [46]. In Fig. 4(c), O1s for the self-doped Ta_2O_5 could be fitted

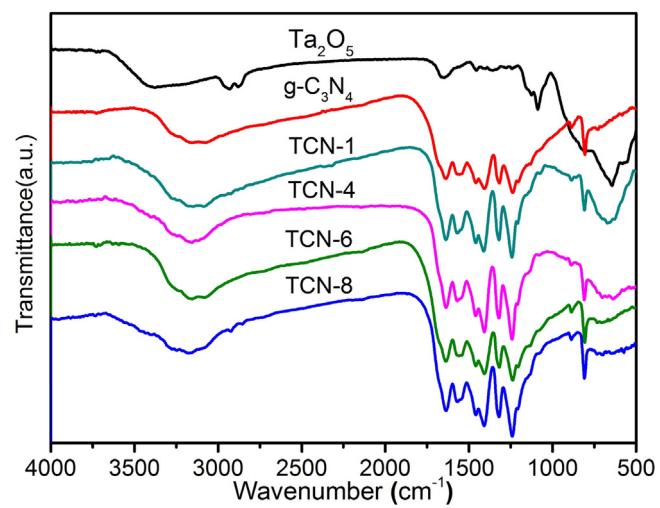


Fig. 3. FT-IR spectra of the self-doped Ta_2O_5 , $\text{g-C}_3\text{N}_4$, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts.

into two peaks at 530.7 and 532.3 eV, which were attributed to the lattice oxygen atoms, oxygen atoms of surface $-\text{OH}$ species and oxygen vacancy neighbors to Ta^{4+} species of the self-doped Ta_2O_5 catalyst [37,47,48]. The binding energies of O1s (530.7, 532.3 eV) of TCN-6 catalyst were slightly higher compared with that of Ta_2O_5 . Interestingly, the binding energies of $\text{Ta}4\text{f}_{7/2}$ and $\text{Ta}4\text{f}_{5/2}$ for TCN-6 catalyst (26.5, 28.4 eV) (Fig. 4(d)) were also higher compared with those of the self-doped Ta_2O_5 and TCN-mix, further confirming the formation of new chemical bond $\text{Ta}-\text{O}-\text{C}$ in TCN-6 catalyst [27,37,38,49]. In literatures, $\text{Ti}-\text{O}-\text{C}$ chemical bond was often thought to be formed because of the peaks of $\text{Ti}(2\text{p}_{1/2})$ and $\text{Ti}(2\text{p}_{3/2})$ shifting towards a higher binding energy [38,50], while the chemical bonds in the $\text{g-C}_3\text{N}_4/\text{NaNbO}_3$ catalyst was also thought to be formed because the binding energies of $\text{Nb}3\text{d}_{3/2}$, $\text{Nb}3\text{d}_{5/2}$, and O1s of $\text{g-C}_3\text{N}_4/\text{NaNbO}_3$ decreased compared with that of the pure NaNbO_3 [51]. Besides, the $\text{Ta}4\text{f}_{7/2}$ peak of the as-prepared Ta_2O_5

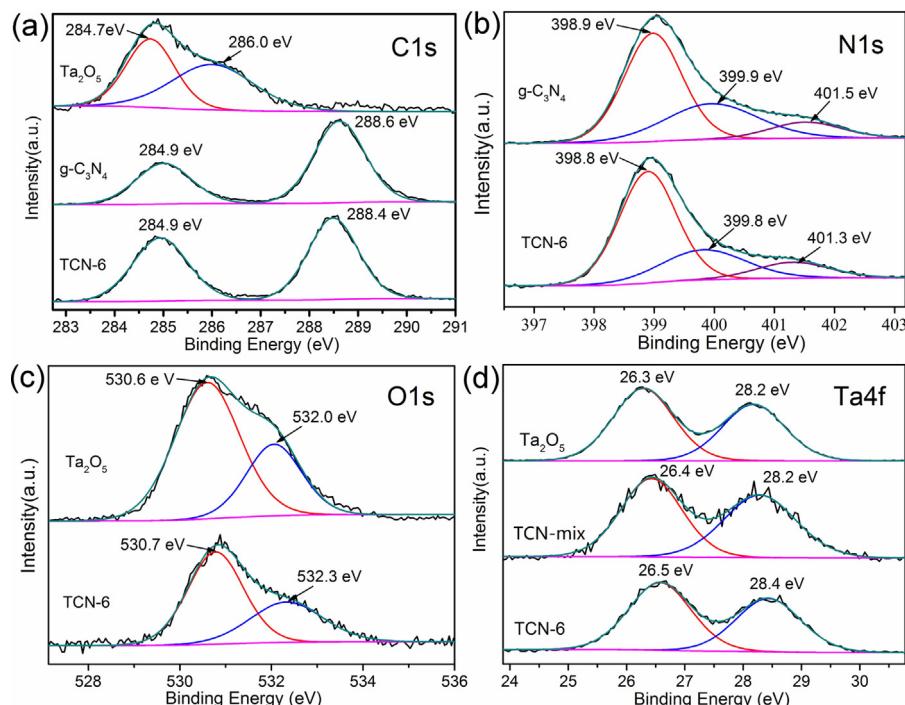


Fig. 4. XPS spectra of the self-doped Ta_2O_5 , $\text{g-C}_3\text{N}_4$, TCN-mix and TCN catalysts: (a) C1s, (b) N1s, (c) O1s and (d) Ta 4f.

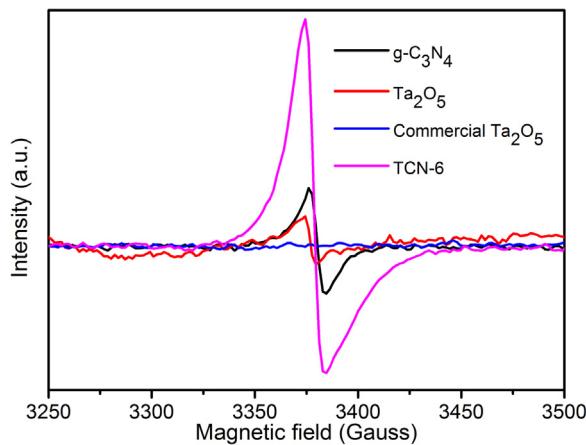


Fig. 5. EPR spectra of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 , commercial Ta_2O_5 , and TCN catalysts.

(26.3 eV) was lower than that of the non-defect Ta_2O_5 reported in literature [52], indicating the formation of Ta^{4+} species neighbors to oxygen vacancy in the self-doped Ta_2O_5 [47,53], as discussed below. Based on the above analyses, it could be concluded that TCN catalyst was successfully fabricated by forming $\text{Ta}-\text{O}-\text{C}$ bond rather than the simple physical mixture.

EPR measurements were conducted to further investigate the oxygen vacancy defects (or Ta^{4+} species) of $\text{g-C}_3\text{N}_4$, commercial Ta_2O_5 , the self-doped Ta_2O_5 , and TCN catalysts. As shown in Fig. 5, the commercial Ta_2O_5 showed no detectable EPR signals, whereas the as-prepared Ta_2O_5 quantum dots displayed a strong EPR signal at about $g = 2.085$, which could be attributed to oxygen vacancy (Ov.) defects (Ta^{4+} species) in the as-prepared Ta_2O_5 , because Ta^{4+} species was often thought to be produced as well as oxygen vacancy (Ov.) generation [47,54]. The $\text{g-C}_3\text{N}_4$ showed an EPR signal at about $g = 2.083$, which was corresponding to the uncoupled electron of the skeleton CN aromatic rings [24]. The highly enhanced EPR signal in intensity of TCN catalyst was observed at $g = 2.084$, which indicated that the $\text{Ta}-\text{O}-\text{C}$ chemical bond contributed to the existence of Ta^{4+} species in the TCN catalyst.

Fig. 6 displayed the UV-vis absorbance spectrum, the colors (insert) and the estimated bandgap of the commercial Ta_2O_5 , the self-doped Ta_2O_5 , $\text{g-C}_3\text{N}_4$, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts. As displayed in Fig. 6(a), the commercial Ta_2O_5 exhibited strong UV absorption with a spectrum absorption edge of ~ 320 nm, and the estimated bandgap of the commercial Ta_2O_5 is about 3.95 eV, which was consistent with the literature [11]. However, the self-doped Ta_2O_5 showed a strong visible light absorption, which was induced by Ta^{4+} species in self-doped Ta_2O_5 [35], showing great advantages compared with those of commercial Ta_2O_5 , and the estimated bandgap of the as-prepared Ta_2O_5 in this experiment was ~ 2.78 eV, much lower than that of commercial Ta_2O_5 (Fig. 6(b)), which indicated that the self-doped Ta_2O_5 were likely to have visible light activities. Besides, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts also displayed strong visible light absorption from 400 to 800 nm, mainly because of the existence of $\text{g-C}_3\text{N}_4$ [55]. And the estimated bandgaps of TCN-1, TCN-4, TCN-6 and TCN-8 catalysts were about 2.753, 2.759, 2.765, 2.770 eV, which were higher than that of $\text{g-C}_3\text{N}_4$ (~ 2.75 eV) yet much lower than that of the commercial Ta_2O_5 (3.95 eV). Besides, the spectral absorption edge of TCN-1, TCN-4, TCN-6 and TCN-8 had a distinct blue shift in comparison to that of $\text{g-C}_3\text{N}_4$, mainly because of the formation of $\text{Ta}-\text{O}-\text{C}$ chemical bond between the self-doped Ta_2O_5 and cotton-like $\text{g-C}_3\text{N}_4$.

The PL emission spectra of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 , TCN-1, TCN-4, TCN-6 and TCN-8 catalysts excited by 350 nm ultraviolet light were measured to study the trapping, migration, and

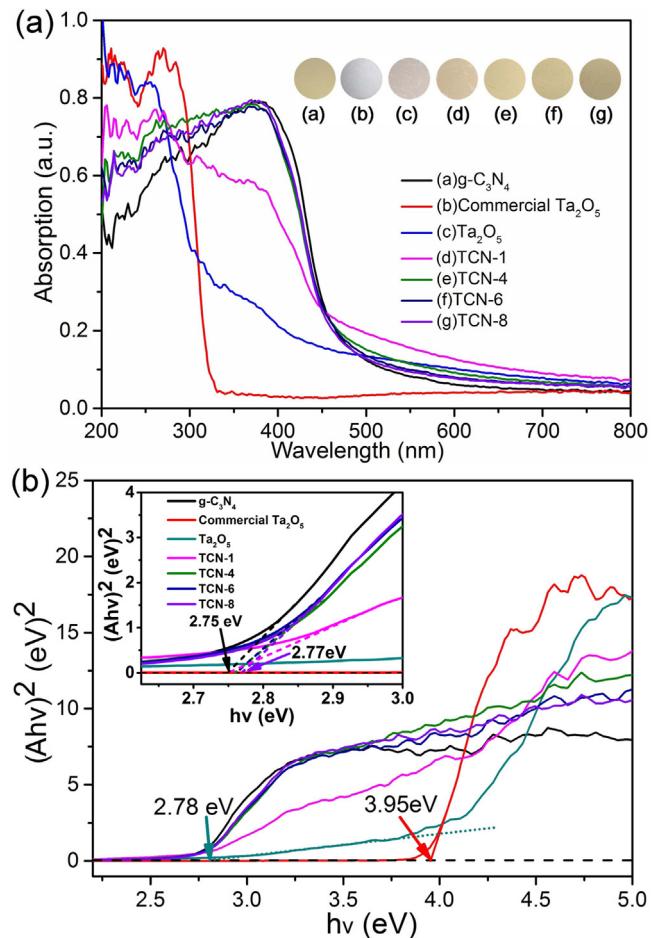


Fig. 6. UV-vis absorption spectra, the colors (insert) and estimated bandgaps of the self-doped Ta_2O_5 , $\text{g-C}_3\text{N}_4$, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts.

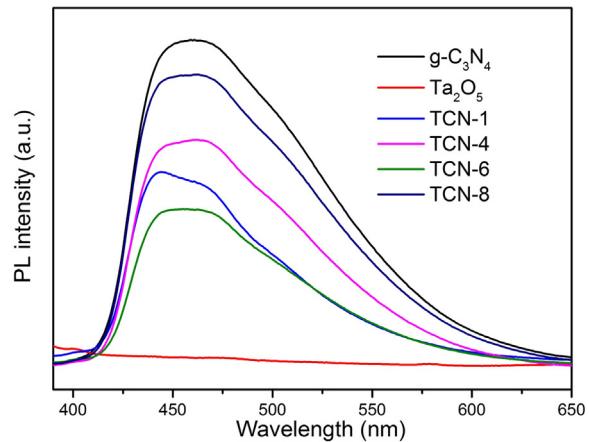


Fig. 7. Photoluminescent spectra of $\text{g-C}_3\text{N}_4$, the self-doped Ta_2O_5 , TCN-1, TCN-4, TCN-6 and TCN-8 catalysts.

recombination of the photo-induced electrons and holes at room temperature [37,56]. As shown in Fig. 7, the PL emission spectra of $\text{g-C}_3\text{N}_4$ presented a strong band-band emission from ~ 390 to 650 nm, indicating the rapid recombination of the photo-induced electrons and holes, which was detrimental for enhancement of the charge separation efficiency. However, the PL intensity of TCN catalysts significantly decreased, and TCN-6 displayed the lowest PL intensity, indicating that the recombination of the photo-induced electrons and holes was highly suppressed because of the formation

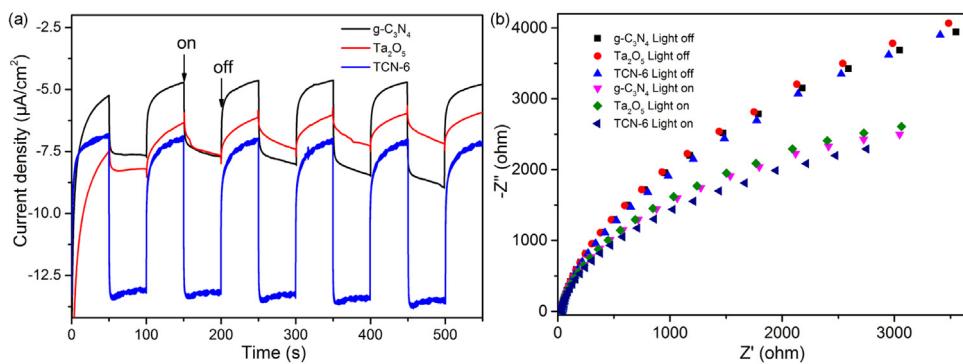


Fig. 8. Photocurrent response (a) and electrochemical impedance spectra (b) of g-C₃N₄, the self-doped Ta₂O₅, TCN-6 catalysts under visible light irradiation ($\lambda > 420$ nm) at 0.1 V vs. Ag/AgCl in 0.1 M Na₂SO₄ solution.

of Ta—O—C bond and Ta⁴⁺ species, which benefited of the excited electrons easily transferring into the interface between cotton-like g-C₃N₄ and Ta₂O₅ [14,57,58]. And thus, it was the formation of Ta—O—C chemical bond and Ta⁴⁺ species between the self-doped Ta₂O₅ and cotton-like g-C₃N₄ that highly promoted the charge separation.

In order to further investigate the interfacial charge separation and charge transfer resistance of g-C₃N₄, the self-doped Ta₂O₅ and TCN catalyst, photocurrent transient response and electrochemical impedance spectra were determined under visible light irradiation ($\lambda > 420$ nm) with a three-compartment cell. In general, the enhanced photocurrent response and small arc radius often represented a higher separation efficiency of photo-induced electron and photo-induced hole pairs and lower charge transfer resistance [59]. As shown in Fig. 8(a), the generated photocurrent of g-C₃N₄, the self-doped Ta₂O₅ and TCN-6 catalysts displayed a reproducible response during the light source on/off cycles. And TCN-6 catalyst displayed the strongest photocurrent transient response to compare with those of g-C₃N₄ and the self-doped Ta₂O₅, which indicated the photo-induced electrons and holes could effectively separate and transfer under visible light irradiation ($\lambda > 420$ nm) [60]. As depicted in Fig. 8(b), the arc radii of g-C₃N₄, the self-doped Ta₂O₅ and TCN-6 catalysts under visible light irradiation was much smaller than those of g-C₃N₄, the self-doped Ta₂O₅ and TCN-6 catalysts without irradiation, indicating smaller charge transfer resistance, lower recombination of photo-induced electrons and photo-induced holes and higher charge separation efficiency under visible light irradiation [57,61]. Besides, TCN-6 catalyst displayed the smallest arc radius, indicating the smallest charge transfer resistance and highest charge separation efficiency under visible light irradiation, which further confirmed that the formation of Ta—O—C chemical bond in TCN catalyst highly enhanced the charge separation between the self-doped Ta₂O₅ and cotton-like g-C₃N₄.

Fig. 9 showed the photocatalytic hydrogen evolution activities of the self-doped Ta₂O₅, g-C₃N₄, TCN-mix, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts and further confirmed the enhancement of the photocatalytic activity of TCN catalyst to compare with those of the self-doped Ta₂O₅, g-C₃N₄ and the g-C₃N₄-based photocatalysts in table S1 (Supporting information). As depicted in Fig. 9(a), the hydrogen production rate of the self-doped Ta₂O₅ could reach 7.98 μmol g⁻¹ h⁻¹ because of the formation of Ta⁴⁺ defect energy level in the Ta₂O₅, while the commercial Ta₂O₅ displayed no visible light photocatalytic activity. The pure g-C₃N₄ showed a hydrogen evolution rate of 169.45 μmol g⁻¹ h⁻¹, much lower than those of all the TCN catalysts. And TCN-6 catalyst displayed the highest photocatalytic hydrogen evolution activity (624.99 μmol g⁻¹ h⁻¹), also higher than that of g-C₃N₄ calcined by the second time at 500 °C for 3 h (~282.07 μmol g⁻¹ h⁻¹), which also indicated that the highly enhanced photocatalytic activities of TCN catalysts were mainly

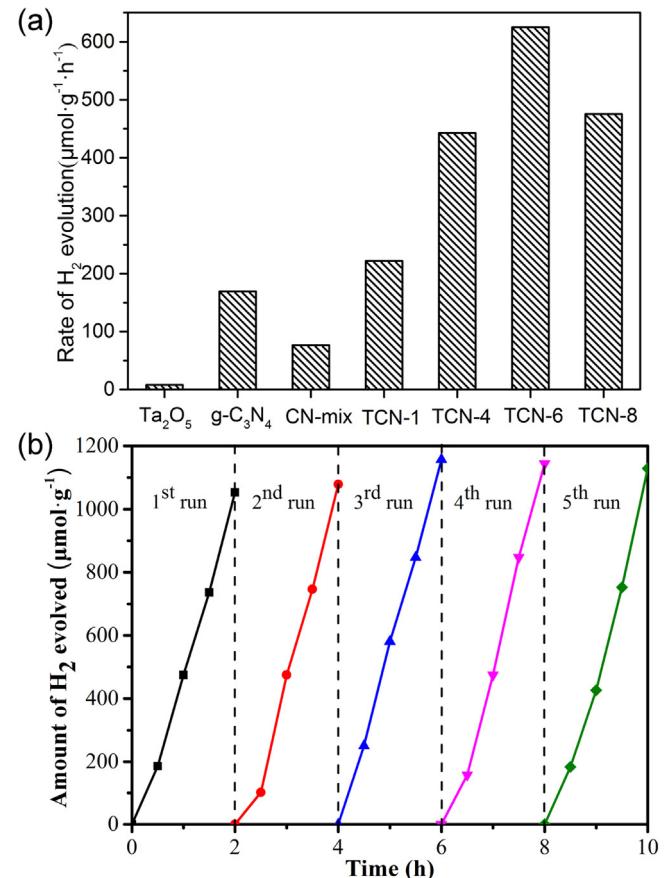


Fig. 9. The photocatalytic hydrogen evolution rate of the self-doped Ta₂O₅, g-C₃N₄, TCN-mix, TCN-1, TCN-4, TCN-6 and TCN-8 catalysts, and recyclable photocatalytic activity of TCN-6 catalyst.

attributed to the doping effects of the self-doped Ta₂O₅ quantum dots, though the secondary calcination of g-C₃N₄ in a ceramic crucible with a cover was also favorable for the increase of the photocatalytic activity [62]. And thus, we could conclude that Ta₂O₅ quantum dots played a crucial role for enhancing the photocatalytic activities of TCN catalysts. Besides, all the photocatalytic hydrogen evolution activities of TCN catalysts were much higher than that of TCN-mix (6:1 sample), mainly because of the formation of Ta—O—C chemical bond between the self-doped Ta₂O₅ and g-C₃N₄ rather than the only simple physical mixture. We also investigated the photocatalytic stability of TCN-6 catalyst for photocatalytic hydrogen evolution under visible light irradiation. As shown in Fig. 9 (b),

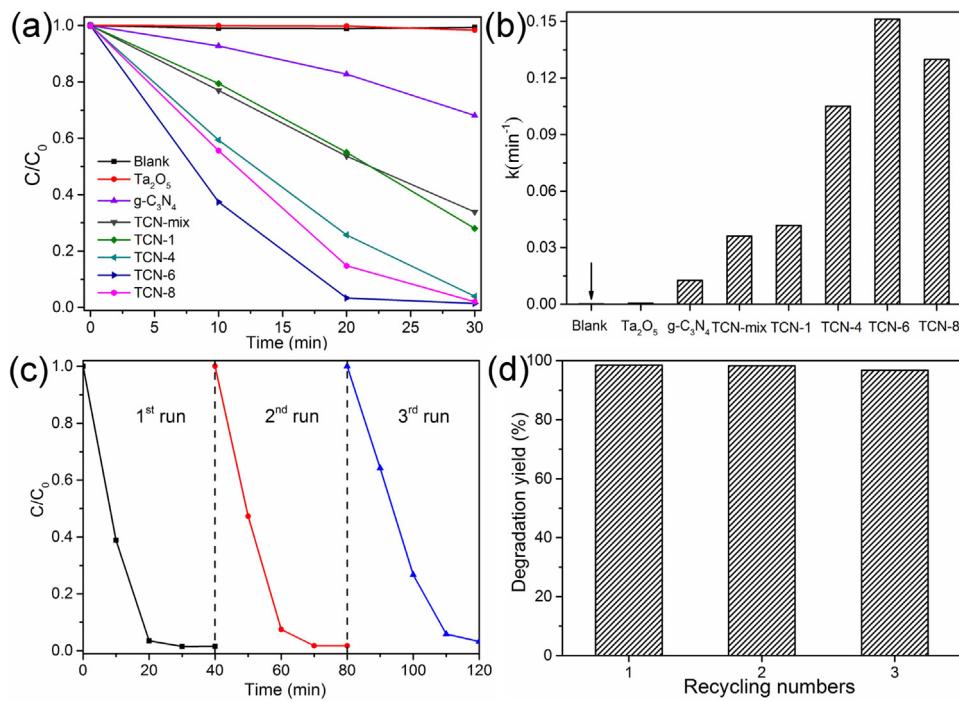


Fig. 10. Photocatalytic activities (a), the rate constant (b), three recyclable runs (c) of TCN-6 catalyst and the degradation yield (d) of TCN-6 catalyst for RhB degradation.

TCN-6 catalyst still displayed excellent photocatalytic activity even after five recyclable tests.

We also carried out the photocatalytic RhB degradation of TCN catalysts under visible light irradiation to evaluate the charge separation between the self-doped Ta_2O_5 and cotton-like $g-C_3N_4$. Fig. 10(a) showed the photocatalytic RhB degradation curves for 30 min. The pure $g-C_3N_4$ displayed relatively poor visible light degradation activity compared with those of all the TCN catalysts. Besides, almost all the RhB could be removed in about 20 min for TCN-6 catalyst, much faster than those of TCN-mix, $g-C_3N_4$, the self-doped Ta_2O_5 , and the $g-C_3N_4$ -based catalysts in table S2 (Supporting information), further confirming the formation of the Ta–O–C chemical bond rather than simple physical mixture. The apparent rate constants k were 0.0418, 0.1052, 0.1512 and 0.1299 min⁻¹ for TCN-1, TCN-4, TCN-6 and TCN-8 catalysts, while the apparent rate constant k of the self-doped Ta_2O_5 and $g-C_3N_4$ were only 0.0005328 and 0.0127 min⁻¹, which further confirmed the important role of the Ta–O–C chemical bond for the separation of the photo-induced electron and hole pairs, as depicted in Fig. 10(b). A reported apparent rate constant k of $g-C_3N_4$ -ZnO composite for photodegradation of methyl orange was 0.0360 min⁻¹, and another reported maximum apparent rate constant of $GdVO_4/g-C_3N_4$ photocatalyst for RhB photodegradation was only 0.0434 min⁻¹, much lower than that of TCN photocatalyst [63,64], which indicated TCN photocatalyst was an efficient photocatalyst for RhB degradation under visible light irradiation. As shown in Fig. 10(c), three recycling runs clearly revealed the good photochemical stability of TCN-6 catalyst for photocatalytic RhB degradation, and all the degradation yields were more than 96.76% (Fig. 10(d)). Based on the above analysis, TCN photocatalyst could be as a promising visible light photocatalyst for pollutant removal.

In order to investigate the roles of the hydroxyl radicals and holes in the RhB oxidation under visible light irradiation, the trapping experiments of TCN-6 catalyst by adding different sacrificial agents were conducted. As reported in literatures [65–67], ammonium oxalate and isopropanol could be used as the hole scavenger and $\bullet OH$ quencher in the organic dyes degradation process, respectively. As shown in Fig. 11, almost all the RhB could be

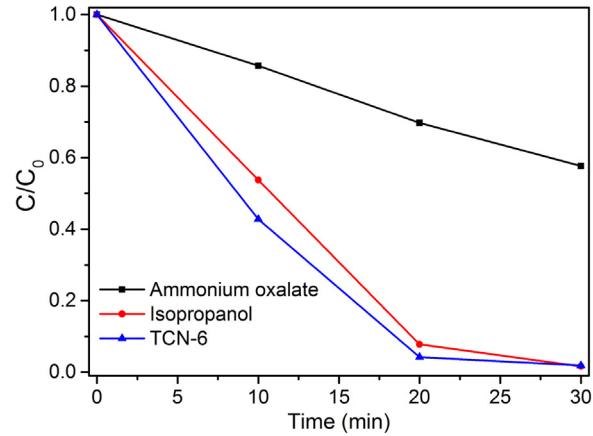
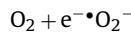
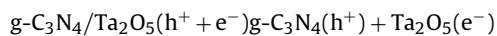
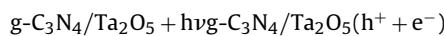


Fig. 11. The active species trapping experiment of TCN-6 catalyst.

removed in about 20 min without adding any hole scavenger and $\bullet OH$ quencher, also consistent with the above RhB degradation test. However, when ammonium oxalate was added into the RhB solution, the degradation rate of RhB was greatly suppressed, while it was barely affected in presence of isopropanol, which strongly indicated that RhB degradation with TCN catalyst could be mainly attributed to direct hole oxidation [33,66]. And holes were the main active species in the RhB degradation for TCN catalyst under visible light irradiation. The degradation reaction in this experiment seemed much like $g-C_3N_4/TiO_2$ [68] in RhB degradation and could be described as follows,



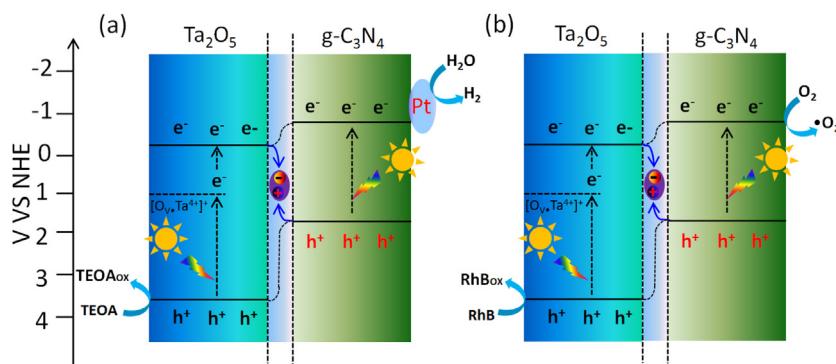


Fig. 12. Proposed direct Z-scheme mechanisms of TCN catalyst for (a) hydrogen production and (b) RhB degradation.

Based on the above analyses, possible direct Z-scheme mechanisms of TCN catalyst for hydrogen production and RhB degradation were proposed in Fig. 12. Ta^{4+} species was produced as well as the oxygen vacancy generation [47], and the oxygen vacancy (Ta^{4+} species) could have visible light response of the wide bandgap Ta_2O_5 with a hydrogen production rate of $7.98 \mu\text{mol g}^{-1} \text{h}^{-1}$, showing its great advantage to compare with that of the commercial Ta_2O_5 . In this experiment, the highly enhanced photocatalytic activities of TCN catalyst could be ascribed to the formation Ta^{4+} species and the Ta–O–C chemical bond, which highly promoted the charge separation for hydrogen production and RhB degradation. The conduction band of $g\text{-C}_3\text{N}_4$ (-0.90 eV) was more negative compared with that of Ta_2O_5 (-0.17 eV) [69] and H^+/H_2 (0 eV). And the reduction potential of O_2/O_2^- was -0.33 eV [70], more negative than the conduction band of Ta_2O_5 but positive than that of $g\text{-C}_3\text{N}_4$. And thus, the electrons of conduction band of $g\text{-C}_3\text{N}_4$ had stronger reducibility than that of Ta_2O_5 , and could react with dissolved O_2 to form O_2^- or H_2O for hydrogen production, but the electrons of conduction band of Ta_2O_5 did not because of the weaker reducibility [71]. And the photo-induced electrons of the conduction band of $g\text{-C}_3\text{N}_4$ were likely to transfer to reaction active site for the reduction of H_2O or O_2 dissolved in RhB solution to generate H_2 or O_2^- species, while the electrons from the valence band of the Ta^{4+} doped Ta_2O_5 leaped into Ta^{4+} defect energy level under visible light irradiation and then transferred to the conduction band of Ta_2O_5 to react with the holes from the valence band of $g\text{-C}_3\text{N}_4$ at the interface defect sites, as illustrated in Fig. 11. The holes of the valence band of Ta_2O_5 were removed by TEOA oxidation or RhB degradation, which was also supported by the active species trapping experiment of TCN-6 catalyst. It was the formation of Ta–O–C chemical bond and Ta^{4+} defect energy level that effectively promoted charge separation between the self-doped Ta_2O_5 and cotton-like $g\text{-C}_3\text{N}_4$, and highly enhanced the photocatalytic activity of TCN catalysts for hydrogen evolution and RhB degradation.

4. Conclusions

We successfully prepared a novel Ta^{4+} self-doped Ta_2O_5 quantum dots and the self-doped Ta_2O_5 quantum dots modified cotton-like $g\text{-C}_3\text{N}_4$ nanosheet by vapor hydrolysis reaction and calcining treatment for the first time. The as-prepared self-doped Ta_2O_5 showed excellent visible light response from 400 nm to 800 nm and the amazing visible light photocatalytic activity for hydrogen production, mainly because of the formation of Ta^{4+} defect energy level in the self-doped Ta_2O_5 . Besides, TCN photocatalyst displayed highly enhanced photocatalytic activities for hydrogen production and RhB degradation under visible light irradiation ($\lambda > 420 \text{ nm}$), indicating the higher charge separation efficiency in comparison to those of the self-doped Ta_2O_5 and

cotton-like $g\text{-C}_3\text{N}_4$. And it was the strong synergistic interactions of Ta–O–C chemical bond and Ta^{4+} defect energy level between the self-doped Ta_2O_5 and cotton-like $g\text{-C}_3\text{N}_4$ that highly enhanced the photocatalytic activity of TCN catalyst.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.12.040>.

The SEM and high magnification TEM images of the as-prepared TCN-6 catalyst are shown in Fig. S1, and some recent studies on $g\text{-C}_3\text{N}_4$ -based photocatalysts for hydrogen production and RhB degradation are shown in Table S1 and S2, which could be found in the online version.

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.
- [2] X. Chen, S. Shen, L. Guo, S.S. Mao, *Chem. Rev.* 110 (2010) 6503–6570.
- [3] K. Maeda, K. Teramura, D.L. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* 440 (2006), 295–295.
- [4] J.L. Gong, R. Luque, *Chem. Soc. Rev.* 43 (2014) 7466–7468.
- [5] A. Kudo, Y. Misaki, *Chem. Soc. Rev.* 38 (2009) 253–278.
- [6] P. Zhang, T. Wang, J. Gong, *Adv. Mater.* 27 (2015) 5328–5342.
- [7] S.G. Kumar, L.G. Devi, *J. Phys. Chem. A* 115 (2011) 13211–13241.
- [8] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *Chem. Rev.* 114 (2014) 9824–9852.
- [9] C. Wang, D. Astruc, *Chem. Soc. Rev.* 43 (2014) 7188–7216.
- [10] L. Dai, Y. Xue, L. Qu, H.-J. Choi, J.-B. Baek, *Chem. Rev.* 115 (2015) 4823–4892.
- [11] Y. Luo, X. Liu, X. Tang, Y. Luo, Q. Zeng, X. Deng, S. Ding, Y. Sun, *J. Mater. Chem. A* 2 (2014) 14927–14939.
- [12] C. Zhou, L. Shang, H. Yu, T. Bian, L.-Z. Wu, C.-H. Tung, T. Zhang, *Catal. Today* 225 (2014) 158–163.
- [13] L. Xu, W. Shi, J. Guan, *Catal. Commun.* 25 (2012) 54–58.
- [14] J. Wang, J. Huang, H. Xie, A. Qu, *Int. J. Hydrogen Energy* 39 (2014) 6354–6363.
- [15] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong, Z. Kang, *Science* 347 (2015) 970–974.
- [16] J. Zhang, X. Chen, K. Takanabe, K. Maeda, K. Domen, J.D. Epping, X. Fu, M. Antonietti, X. Wang, *Angew. Chem. Int. Ed.* 49 (2010) 441–444.
- [17] M. Zhang, W.J. Jiang, D. Liu, J. Wang, Y.F. Liu, Y.Y. Zhu, Y.F. Zhu, *Appl. Catal. B-Environ.* 183 (2016) 263–268.
- [18] J. Lin, Z. Pan, X. Wang, A.C.S. Sustain. Chem. Eng. 2 (2014) 353–358.
- [19] F. Dong, M. Ou, Y. Jiang, S. Guo, Z. Wu, *Ind. Eng. Chem. Res.* 53 (2014) 2318–2330.
- [20] A.B. Jorge, D.J. Martin, M.T.S. Dhanoa, A.S. Rahman, N. Makwana, J. Tang, A. Sella, F. Cora, S. Firth, J.A. Darr, P.F. McMillan, *J. Phys. Chem. C* 117 (2013) 7178–7185.
- [21] S. Chu, Y. Wang, Y. Guo, J. Feng, C. Wang, W. Luo, X. Fan, Z. Zou, *ACS Catal.* 3 (2013) 912–919.

[22] W.J. Ong, L.L. Tan, Y.H. Ng, S.T. Yong, S.P. Chai, *Chem. Rev.* 116 (2016) 7159–7329.

[23] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, *Nature Mater.* 8 (2009) 76–80.

[24] J. Zhang, M. Zhang, R.-Q. Sun, X. Wang, *Angew. Chem. Int. Ed.* 51 (2012) 10145–10149.

[25] Z.A. Lan, G.G. Zhang, X.C. Wang, *Appl. Catal. B-Environ.* 192 (2016) 116–125.

[26] J. Xue, S. Ma, Y. Zhou, Z. Zhang, M. He, *Acs Appl. Mater. Inter.* 7 (2015) 9630–9637.

[27] N. Tian, H. Huang, C. Liu, F. Dong, T. Zhang, X. Du, S. Yu, Y. Zhang, *J. Mater. Chem. A* 3 (2015) 17120–17129.

[28] W.J. Ong, L.K. Putri, L.L. Tan, S.P. Chai, S.T. Yong, *Appl. Catal. B-Environ.* 180 (2016) 530–543.

[29] J. Liu, S. Wen, Y. Hou, F. Zuo, G.J.O. Beran, P. Feng, *Angew. Chem. Int. Ed.* 52 (2013) 3241–3245.

[30] X. Dong, F. Cheng, *J. Mater. Chem. A* 3 (2015) 23642–23652.

[31] S.C. Yan, Z.S. Li, Z.G. Zou, *Langmuir* 25 (2009) 10397–10401.

[32] F. Dong, Z. Zhao, T. Xiong, Z. Ni, W. Zhang, Y. Sun, W.-K. Ho, *ACS Appl. Mater. Inter. Interfaces* 5 (2013) (1401) 11392–11401.

[33] N. Tian, H. Huang, Y. He, Y. Guo, T. Zhang, Y. Zhang, *Dalton Trans.* 44 (2015) 4297–4307.

[34] W.-J. Ong, L.-L. Tan, S.-P. Chai, S.-T. Yong, A.R. Mohamed, *Nano Energy* 13 (2015) 757–770.

[35] X. Wu, S. Yin, B. Liu, M. Kobayashi, M. Kakihana, T. Sato, *J. Mater. Chem. A* 2 (2014) 20832–20840.

[36] X. Wu, S. Yin, Q. Dong, T. Sato, *Phys. Chem. Chem. Phys.* 15 (2013) 20633–20640.

[37] M. Xu, L. Han, S. Dong, *Acs Appl. Mater. Interfaces* 5 (2013) 12533–12540.

[38] H. Yu, Y. Zhao, C. Zhou, L. Shang, Y. Peng, Y. Cao, L.-Z. Wu, C.-H. Tung, T. Zhang, *J. Mater. Chem. A* 2 (2014) 3344–3351.

[39] Y.J. Wang, R. Shi, J. Lin, Y.F. Zhu, *Energ. Environ. Sci.* 4 (2011) 2922–2929.

[40] R.V. Goncalves, R. Wojcieszak, P.M. Uberman, S.R. Teixeira, L.M. Rossi, *Phys. Chem. Chem. Phys.* 16 (2014) 5755–5762.

[41] J.Y. Zhang, B. Lim, I.W. Boyd, *Thin Solid Films* 336 (1998) 340–343.

[42] J.Y. Zhang, B. Lim, I.W. Boyd, *Appl. Surf. Sci.* 154 (2000) 382–386.

[43] X. She, H. Xu, H. Wang, J. Xia, Y. Song, J. Yan, Y. Xu, Q. Zhang, D. Du, H. Li, *T. Dalton.* (2015) 7021–7031.

[44] B. Neumann, P. Bogdanoff, H. Tributsch, S. Sakthivel, H. Kisch, *J. Phys. Chem. B* 109 (2005) 16579–16586.

[45] M. Lu, Z. Pei, S. Weng, W. Feng, Z. Fang, Z. Zheng, M. Huang, P. Liu, *Phys. Chem. Chem. Phys.* 16 (2014) 21280–21288.

[46] J. Lv, T. Kako, Z. Li, Z. Zou, J. Ye, *J. Phys. Chem. C* 114 (2010) 6157–6162.

[47] M. Xing, W. Fang, M. Nasir, Y. Ma, J. Zhang, M. Anpo, *J. Catal.* 297 (2013) 236–243.

[48] Y. Zhou, C. Chen, N. Wang, Y. Li, H. Ding, *J. Phys. Chem. C* 120 (2016) 6116–6124.

[49] H. Wang, X.Z. Yuan, H. Wang, X.H. Chen, Z.B. Wu, L.B. Jiang, W.P. Xiong, G.M. Zeng, *Appl. Catal. B-Environ.* 193 (2016) 36–46.

[50] Y. Cong, X. Li, Y. Qin, Z. Dong, G. Yuan, Z. Cui, X. Lai, *Appl. catal. B-Environ.* 107 (2011) 128–134.

[51] H. Shi, G. Chen, C. Zhang, Z. Zou, *ACS Catal.* 4 (2014) 3637–3643.

[52] W.J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J.N. Kondo, M. Hara, M. Kawai, Y. Matsumoto, K. Domen, *J. Phys. Chem. B* 107 (2003) 1798–1803.

[53] M. Xing, J. Zhang, F. Chen, B. Tian, *Chem. Commun.* 47 (2011) 4947–4949.

[54] E. Lira, S. Wendt, P. Huo, J.O. Hansen, R. Streber, S. Porsgaard, Y. Wei, R. Bechstein, E. Laegsgaard, F. Besenbacher, *J. Am. Chem. Soc.* 133 (2011) 6529–6532.

[55] C. Han, Y. Wang, Y. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, *Nano Res.* 8 (2015) 1199–1209.

[56] K. Li, S. Gao, Q. Wang, H. Xu, Z. Wang, B. Huang, Y. Dai, J. Lu, *Acs Appl. Mater. Inter.* 7 (2015) 9023–9030.

[57] H.Q. Li, Y.X. Liu, Y.M. Cui, W.B. Zhang, C. Fu, X.C. Wang, *Appl. Catal. B-Environ.* 183 (2016) 426–432.

[58] X.J. Bai, R.L. Zong, C.X. Li, D. Liu, Y.F. Liu, Y.F. Zhu, *Appl. Catal. B-Environ.* 147 (2014) 82–91.

[59] S.L. Ma, S.H. Zhan, Y.N. Jia, Q. Shi, Q.X. Zhou, *Appl. Catal. B-Environ.* 186 (2016) 77–87.

[60] C.D. Lv, G. Chen, J.X. Sun, Y.S. Zhou, S. Fan, C.M. Zhang, *Appl. Catal. B-Environ.* 179 (2015) 54–60.

[61] M. Zhang, W.Q. Yao, Y.H. Lv, X.J. Bai, Y.F. Liu, W.J. Jiang, Y.F. Zhu, *J. Mater. Chem. A* 2 (2014) 11432–11438.

[62] P. Niu, L. Zhang, G. Liu, H.-M. Cheng, *Adv. Funct. Mater.* 22 (2012) 4763–4770.

[63] J.-X. Sun, Y.-P. Yuan, L.-G. Qiu, X. Jiang, A.-J. Xie, Y.-H. Shen, J.-F. Zhu, *Dalton Trans.* 41 (2012) 6756–6763.

[64] Y. He, J. Cai, T. Li, Y. Wu, H. Lin, L. Zhao, M. Luo, *Chem. Eng. J.* 215 (2013) 721–730.

[65] J. Wu, J. Wang, H. Li, Y. Du, X. Jia, B. Liu, *CrystEngComm* 16 (2014) 9675–9684.

[66] S. Chen, Y. Hu, S. Meng, X. Fu, *Appl. Catal. B-Environ.* 150 (2014) 564–573.

[67] J. Zhuang, W. Dai, Q. Tian, Z. Li, L. Xie, J. Wang, P. Liu, X. Shi, D. Wang, *Langmuir* 26 (2010) 9686–9694.

[68] R. Hao, G. Wang, H. Tang, L. Sun, C. Xu, D. Han, *Appl. Catal. B-Environ.* 187 (2016) 47–58.

[69] K. Maeda, K. Domen, *J. Phys. Chem. Lett.* 1 (2010) 2655–2661.

[70] Y.C. Deng, L. Tang, G.M. Zeng, J.J. Wang, Y.Y. Zhou, J.J. Wang, J. Tang, Y. Liu, B. Peng, F. Chen, *J. Mol. Catal. A: Chem.* 421 (2016) 209–221.

[71] R.Q. Ye, H.B. Fang, Y.Z. Zheng, N. Li, Y. Wang, X. Tao, *Acs Appl. Mater. Inter.* 8 (2016) 13879–13889.